

THERMOLYTIC CLEAVAGE OF SELECTED ETHER LINKAGES AT MILD TEMPERATURES

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INTRODUCTION

Most discussions of coal structure describe the substance as constituted of aromatic, hydroaromatic and heterocyclic aromatic clusters joined by short aliphatic and ether linkages. Various functional groups including phenolic hydroxyl groups and carboxylic acid groups are also present. Because coals are solids with no recognizable repeating units and generally have limited solubility in all solvents, the enterprise of understanding their structures and relating this understanding to practical purposes, necessarily involves some chemical or physical structure disruption with potential loss of information. Most frequently this has involved thermolysis with hydrogen-donor species present. Recently there has been an increased interest in chemical processing which can be carried out under relatively mild conditions (1) which might be hoped to preserve more of the structural features of the initial material.

Analysis of the materials produced by the processing of coal has tended to focus on carbon-carbon bond breaking. Ether linkages, although believed to be present, have not been considered in detail for their potential role in the thermal or chemical reactions of coal under relatively mild conditions. This is surprising in view of the fact that compounds which model the types of ether moieties which might be present in coals are known to undergo pyrolytic scission at temperatures comparable to those of coal liquefaction (2,3). Moreover, benzyl phenyl ether has been shown to promote hydrogen transfer between tetralin and diphenylmethane under thermolysis conditions (4) suggesting an indirect role for ether structural units in facilitating thermolytic liquefaction. A number of radical chain processes have been suggested

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as explanations for carbon-carbon bond breaking (5-7), and these would require an initiating radical such as an oxygen-center radical produced by ether scission.

Most of the reported studies describing the thermolysis of coal model compounds, ethers in particular, have been performed at much higher temperatures than used in coal liquefaction processes. Obviously, conclusions derived from thermolysis at the higher temperatures cannot be applied directly toward understanding of coal dissolution and/or thermolysis processes. Therefore, we initiated studies on the chemistry of thermolysis of four arylmethyl aryl ethers which undergo thermolysis to a significant extent under relatively mild reaction conditions.

EXPERIMENTAL

Thermolysis experiments were performed in evacuated glass ampoules at reaction temperatures of 250°C to 350°C. In a typical thermolysis experiment, about 50 to 150 mg of the material was sealed in an evacuated glass ampoule (0.5 cm x 10 cm). The sealed ampoule was wrapped with steel wool and then inserted in a tubing bomb reactor of about 10-15 ml capacity. The reactor was then immersed in a heated sand bath for the desired reaction time. Typically, it required less than two minutes to reach the desired reaction temperature. At the end of the experiment, the reactor was immersed in a cold sand bath. Once the reactor had come back to ambient temperature, the sealed tube was removed from the reactor and was cut open to recover its contents. For comparison purposes, some of the thermolysis experiments were also conducted by charging the microautoclave reactor directly with 50 to 150 mg of the material. The products were recovered from the glass ampoule or from the reactor using tetrahydrofuran (THF). The THF solutions containing the reaction products were analyzed by GC and GC-MS equipped with SUPERCAP "High Temperature", Al clad fused silica bonded methyl silicone column (15 m x 0.25 mm id, 0.1 μ m film).

Four ethers, namely, α -naphthylmethyl phenyl ether (α -NMPHE), α -benzyl naphthyl ether (α -BNE), β -naphthylmethyl phenyl ether (β -NMPHE) and β -benzyl naphthyl ether (β -BNE) were prepared by procedures reported in the literature (8,9).

RESULTS AND DISCUSSION

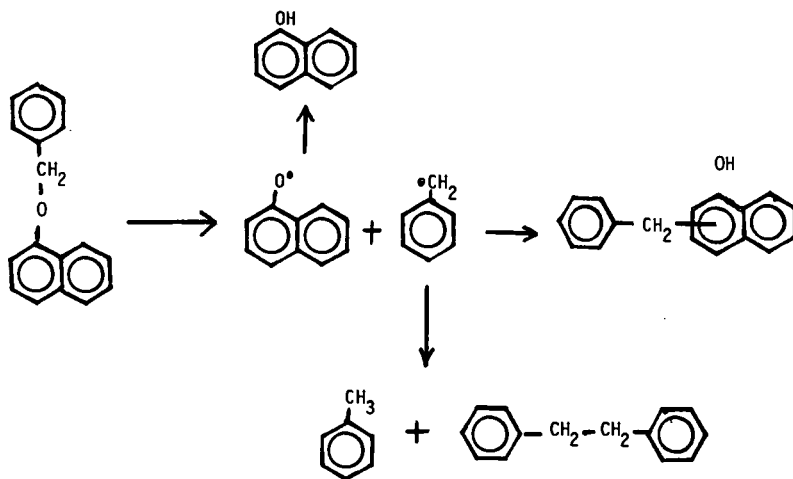
The results of thermolysis of four ethers (α -NMPHE, α -BNE, β -NMPHE, β -BNE) conducted at mild temperatures of 225°C to 350°C with a 30 minute reaction time are given in Table 1 and Figures I and II. Results reported here were calculated based upon the amount of ether left unreacted or decomposed. In order to provide insurance that no appreciable amount of non-volatile product was present, a known amount of triphenylene was added, as an internal standard, during the work up procedure.

As shown by the data in Table 1 and Figures I and II, all the four ethers underwent thermolysis to a significant extent of more than 80% at 325°C or below.

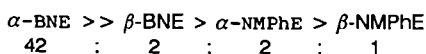
The major products in each case were ArOH, Ar'CH₃, and isomers of the starting ethers which almost certainly have the structures: Ar'CH₂ArOH. Relatively minor amounts of Ar'CH₃CH₂CH₂Ar', Ar'CH=CHAr', Ar'CH₂Ar, and a "dehydrocompound" (parent ion = 232) were also observed. Higher molecular weight materials were found in trace amounts. Isomer yields in sealed tube runs were 30 to 40%, ArOH yields were 20 to 30% and Ar'CH₃ yields were 10 to 30% of GC-observable products.

Formation of observed products could be understood with the help of a typical reaction scheme given below:

THERMOLYSIS OF ALPHA-NAPHTHYL BENZYL ETHER



The relative rates of thermolysis of the four ethers were calculated using the experimental data and were found to be:

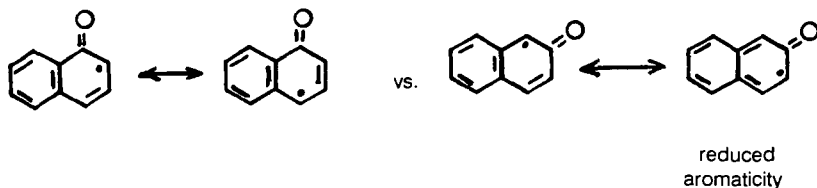


Temp. °C Rate Constant in s⁻¹ x 10⁻⁴ Based on Ether Remaining

	<u>α-BNE</u>	<u>β-BNE</u>	<u>α-NMPHE</u>	<u>β-NMPHE</u>
325	---	17	17	9.4
300	---	2.9	2.3	1.2
285	4.1	0.62	---	0.17
275	7.1	0.34	0.3	---
365	2.6	0.1	---	---

The main conclusion is that the ethers all undergo thermolysis at relatively mild temperatures, presumably by homolysis of the CH₂-O bond followed by recombination of the resultant radicals to give substituted phenols or naphthols or they abstract hydrogen to give ArOH and Ar'CH₃.

An explanation of the relative rates can be found in the relative stabilities of the various radical pairs. Apparently, α -NpCH₂• and β -NpCH₂• differ only slightly in stability whereas α -NpO• is appreciably more stable than β -NpO•. This can be rationalized by assuming that resonance delocalization into the naphthalene ring is much more important in stabilizing NpO• than NpCH₂•. This makes sense because of the instability of oxygen radicals and the strengthening of the C-O bond which results from increasing its C=O character. This analysis also explains why α -NpOCH₂Ph cleaves so much faster than β -NpOCH₂Ph as the α -naphthoxy radical has a contribution of an extra resonance structure:



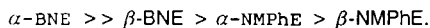
That α -NpOCH₂Ph and β -NpOCH₂Ph should cleave at similar rates is not obvious but the increased stability of α -NpCH₂• relative to PhCH₂• is accidentally equal to the advantage of β -NpO• over PhO•.

A significant difference in product distribution in the thermolysis of α -NMPHE was observed when the reaction vessel was changed from a small glass ampoule (50-150 mg of ether in a 0.5 x 10 cm pyrex ampoule) to a stainless steel pipe reactor (0.5 - 1 g of ether in a 10-15 ml reactor). Relatively larger values of isomers/NpCH₃ + PhOH were observed in the glass vessel. In a previous thermolysis of this ether by Badr and El-Sherief (8) in a sealed glass tube (40 g of ether at 260°C for 7 days), they obtained about the same yield of isomers, but much

more NpCHCH_2Np ($\sim 50\%$). The reasons for these different product distributions are unknown at the present time.

SUMMARY

Thermolysis of four ethers of general structure $\text{Ar}'\text{CH}_2\text{OAr}$, namely, α -naphthylmethyl phenyl ether (α -NMPHE), α -benzyl naphthyl ether (α -BNE), β -naphthylmethyl phenyl ether (β -NMPHE) and β -benzyl naphthyl ether (β -BNE) at mild temperatures of 225°C to 350°C with a 30 minute reaction time was investigated. It was observed that all of the four ethers underwent significant thermolysis to the extent of more than 80% at 325°C or below. The major products in each case were ArOH , $\text{Ar}'\text{CH}_3$, and isomers of the starting ethers. Relatively minor amounts of $\text{Ar}'\text{CH}_2\text{CH}_2\text{Ar}'$, $\text{Ar}'\text{CH}=\text{CHAr}'$, $\text{Ar}'\text{CH}_2\text{Ar}$ and an unknown compound (parent ion = 232) were also observed. Higher molecular weight materials were found in trace amounts. The relative rates of thermolysis were:



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REFERENCES

1. (a) Chawla, B.; Davis, B. Prepr. Pap., Am. Chem. Soc., Div. Fuel Chem., **33**, 440, (1988); (b) Keogh, R. A.; Chawla, B.; Tsai, K. J.; Davis, B. H. ibid., 333; (c) Chawla, B.; Keogh, R.; Davis, B. H. ibid., **32**, 324, (1987); (d) Chawla, B.; Davis, B. H. Fuel Sci. and Tech. Int., **7**, 1, (1988); (e) Chawla, B.; Davis, B. H. Fuel Proc. Tech., accepted, (1989); (f) Chawla, B.; Keogh, R.; Davis, B. Energy & Fuels, in press, (1989); (g) Keogh, R.; Poe, S. H.; Chawla, B., in "Coal Science and Technology", Vol. 11, J. A. Moulijn, K. A. Nater, H. A. G. Chermin, eds., Elsevier, New York, 1987, p. 269; (h) Keogh, R.; Klapheke, J.; Poe, S.; Hardy, R.; Taghizadeh, K.; Medina, R.; Taulbee, D.; Chawla, B.; Tsai, K.; Pollock, D.; Hower, J.; Davis, B. Final Report, Contract No. DE-FC22-86PC90017.
2. Chawla, B.; Davis, B. unpublished results.
3. Larsen, J. W.; Keummerle, E. W. Fuel, **55**, 162, (1976).
4. Sharma, D. K.; Mirza, Z. B. Fuel, **63**, 1329, (1984).
5. Reggel, L.; Raymond, R.; Friedman, S.; Friedel, R. A.; Wender, I. Fuel, **37**, 126, (1958).

6. Stock, L. M.; Malya, N.; Willis, R. S. Proc. Int. Conf. Coal Science, 722, 1985.
7. Sternberg, H. W.; Dolle Donne, C. V.; Pentagees, P.; Moroni, E. C.; Markby, R. E. Fuel, 50, 432, (1971).
8. Badr, M. Z. A.; El-Sherief, H. A. H. Indian Journal of Chemistry, 12, 1067, (1974).
9. Maslak, P.; Guthrie, R. D. J. Am. Chem. Soc., 108, 2637-2640, (1986).

Figure 1. Temperature dependence of the extent of conversion of naphthyl methyl phenyl ether (α , \circ ; β , \bullet).

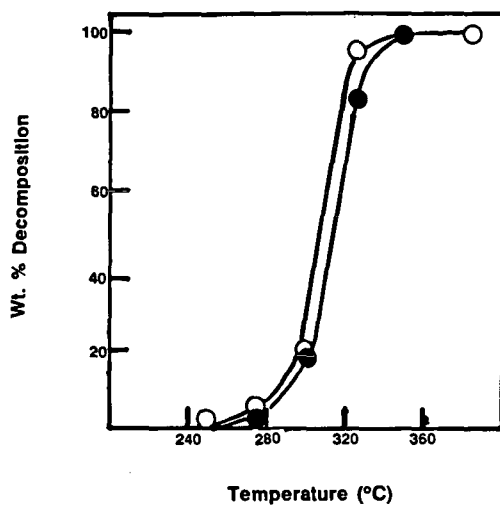


Figure 2. Temperature dependence of the extent of conversion of benzyl naphthyl ether (α , \bullet ; β , \blacksquare).

